Unraveling the mysterious intermediate state in Zr-rich $PbZr_{1-x}Ti_xO_3$

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Antiferroelectric perovskites form an important family of functional electric materials, which have high potential in energy storage and conversion applications. However, a full understanding of their crystal structural formation is still lacking. $PbZrO_3$-based materials can serve as a model system for investigation, not only because $PbZrO_3$ was the first discovered antiferroelectric, but also because it undergoes a typical phase transition sequence from a high-temperature paraelectric to the low-temperature antiferroelectric phase, passing through a possible intermediate (IM) phase that is poorly understood. The IM phases usually exist only in a narrow temperature interval in pure $PbZrO_3$, and therefore it is hard to capture them. On the other hand, with a small amount of Ti substitution, the Zr-rich $PbZr_{1-x}Ti_xO_3$ (PZT, $x \leq 0.06$) also displays a room-temperature antiferroelectric structure and goes through the same phase transition process as $PbZrO_3$. In this case, the temperature range of the IM phase becomes wider, which makes a detailed study of the IM structures possible.

Here we employ a combination of optical and scattering experiments and theoretical calculations to reveal the nature of the intermediate state. Experimental results show that the IM phase is not a pure phase but a state containing a mixture of several short- and long-range correlated structural components that compete energetically in a complicated way. To emphasize this, we shall henceforth refer to it as the IM *state* rather than the IM phase. There are several types of superstructure reflections that appear in the IM state temperature range in the single-crystal diffuse scattering pattern (Fig. 1). With the aid of synchrotron powder total scattering and high-resolution neutron diffraction data analysis, we constructed the complex structural models in this temperature range [1]. Evidence is found that this peculiar state consists of multiple short-range and long-range structural components, as well as complex mesoscopic domain structure [2]. External stimuli such as temperature change or chemical substitution can easily alter each component's energy landscape and thereby change the materials' electrical properties. These findings provide new insights in understanding antiferroelectric-ferroelectric competition and hence in designing new antiferroelectric materials.

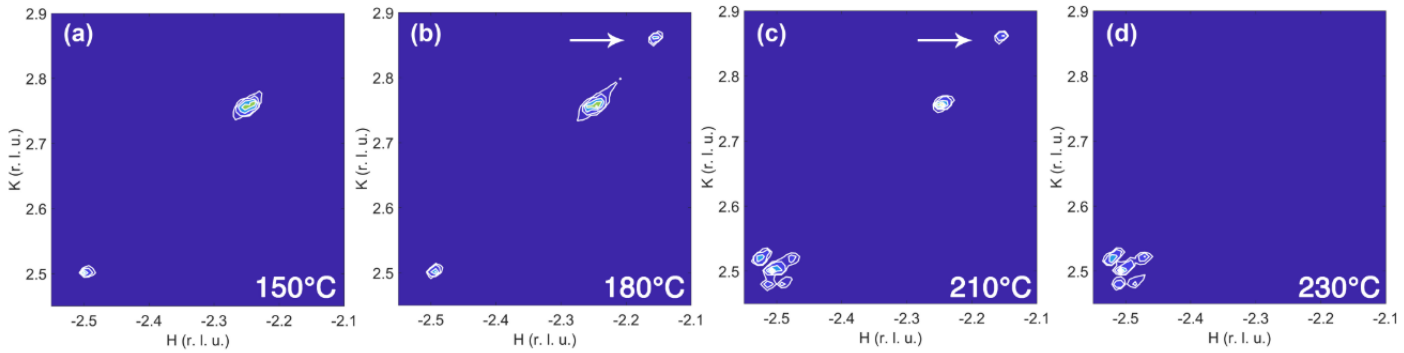

Figure 1. Diffraction patterns and DS intensities during phase-change process of a $PbZr_{0.97}Ti_{0.03}O_3$ crystal. (a)–(d) Data containing M point (–2.5 2.5 0), quarter reflection (–2.25 2.75 0), and IC spot (–2.16 2.84 0) collected at 150 °C, 180 °C, 210 °C, and 230 °C, respectively [1].

[1] An, Z., Yokota, H., Zhang, N., Pasciak, M., Fábry, J., Kopecký, M., Kub, J., Zhang, G., Glazer, A. M., Welberry, T. R., Ren, W., & Ye, Z.-G. (2021) *Phys. Rev. B* **103**, 054113.

[2] An, Z., Xie, S., Zhang, N., Zhuang, J., Glazer, A. M., Ren, W., & Ye, Z.-G. (2021) *APL Mater.* **9**, 030702.

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